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Kinetic Mechanisms for Ionization and Afterburning Suppression

November 1987

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FOREWORD

This final report documents the Air Force Astronautics Laboratory (AFAL) in-house study of kinetic mechanisms for ionization and afterburning suppression. AFAL Project Manager was Dave Weaver.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.
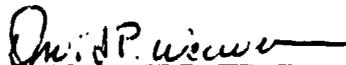
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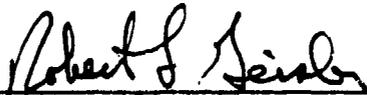
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Currently, very little data exists detailing the chemical mechanisms associated with the addition of suppressants such as K_2SO_4 or KNO_3 and their impact on the production of ions in either typical laboratory flames or solid propellant exhaust flows. On an empirical basis, potassium-bearing salts (K_2SO_4, KNO_2, KCl, etc.) have been found to be among the most general and most effective suppressants. The addition of such alkali metal salts to the plume gases, however, has been observed to increase ion/electron concentrations, which in turn may significantly affect the radar cross section and reduce the motor's performance (e.g., by producing a lower specific impulse). This report summarizes the results of a recent analytical investigation into the influence of the addition of potassium salts on both the inhibition effects and the production electrons in a H_2/Air flame. (H_2/O_2)

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An eleven step reaction mechanism was used for computing the structure of the base hydrogen-oxygen flame. This mechanism has been shown to give good agreement between the computed results and the corresponding experimental data. An additional sixteen step mechanism was added to simulate the influence of potassium inhibition and ionization. The computed concentration profiles of [H] and [OH] show good agreement with experimental data reported in the literature. The influence of KOH addition on the laminar burning velocity, peak OH mole fraction, the rate of fuel and oxidizer decay, the rate of production of product species (including K+ and e-) are presented. Analysis shows that the inhibition effect of K-salts (decrease in burning velocity, peak H and OH mole fraction) increases as the mole fraction of KOH increases in the unburnt mixture. The peak electron mole fraction increases as the inhibition effect of potassium salts increase for both fuel-rich and fuel-lean mixtures. The effect of variation in the rate constants for potassium reactions has been studied. Based on this analysis, two simplified reaction mechanisms (a five step mechanism and an eight step mechanism) are suggested for the inhibition effects.

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INTRODUCTION

The work described in this report stems from the phenomenon in rocket and missile plumes that results from the reignition of the fuel-rich exhaust products mixing with the ambient atmosphere. The secondary flame zone, called afterburning, occurs some distance downstream in the exhaust plume, and generates temperatures typically higher than that of the nozzle exhaust-plane. Therefore, afterburning is a significant source of radiation associated with the rocket in the infrared (IR), visible, and sometimes ultraviolet (UV) spectral regions. Such radiation creates or augments a variety of related general problems: launcher location, early warning, target evasion, and temporary blindness or loss of night vision.

Over the past two decades a variety of substances have been added to rocket and gun propellants in an effort to eliminate or reduce afterburning (or gun muzzle flash), and a variety of compounds have been found to be effective to a greater or lesser extent. However, the physical/chemical mechanisms of afterburning suppression are not completely understood. A suppressant effective in one propellant may not work in another, and the degree of effectiveness cannot be accurately predicted. On an empirical basis, potassium-bearing salts (K_2SO_4, KNO_2, KCl, etc.) have been found to be among the most general and most effective suppressants. The addition of such alkali metal salts to the plume gases, however, has been observed to increase ion/electron concentrations, which in turn may significantly affect the radar cross section and reduce the motor's performance (e.g., by producing a lower specific impulse).

The description of a rocket exhaust as a supersonic jet of hot fuel-rich gases is deceptively simple. The generalized physical phenomenon that it represents, reactive turbulent mixing, is extremely complex. It is not the objective of this report to attempt to solve this general problem or the specific example of rocket afterburning. To approach an understanding of afterburning suppression, it is necessary to assume a phenomenological model based on the available data. As a first approximation, it is possible to identify two aspects of the problem and treat them independently; the first aspect being the gasdynamics of the flow, and the second being the reaction chemistry of the flow.

In this perspective, afterburning and its suppression are conventionally explained as follows. The exhaust gases diffuse and mix turbulently with the

atmosphere. Most of the energy released from the chemical reactions taking place is from hydrogen (from the rocket) and oxygen (from the air) producing water. These reactions are very fast so that the energy is released in a short time period, which in the flow of the plume also means in a relatively small, localized volume of space. This, in turn, causes the temperature in that volume to increase and create what is visually identified as the afterburning flame zone.

Afterburning therefore occurs or does not occur depending on a dynamic balance between competing effects: the diffusion and dilution of the plume flow, and the speed of the oxidation reactions. The radical species that mediate the oxidation of hydrogen (H and OH) are normally in high concentrations in the exhaust plume coming out of a rocket. If these could be significantly reduced, the overall reaction time would be increased. The gases would be more diffused and the volume over which the reaction energy is released would also be increased (nonlinearly) which dictates that the temperature rise would be less. These two conditions will also tend to increase the reaction time, which delays the overall reaction and allows the exothermicity to be dissipated. In the case of potassium, it is hypothesized that radicals are depleted by a set of chain branching reactions involving KOH. Other consistent "explanations" of afterburning suppression exist, notably those involving the participation of suspended particulate material, but the forgoing sequence of events is the most plausible.

Currently, very little data exists detailing the chemical mechanisms associated with the addition of suppressants such as K_2SO_4 or KNO_3 and their impact on the production of ions in either typical laboratory flames or "real world" propellants. This report summarizes the results of a recent analytical investigation into the influence of the addition of potassium salts on the production electrons in a H_2 / Air flame. The kinetic mechanism reported for the addition of KOH to the H_2 - Air flame has been detailed in an earlier report (Ref. 1).

INHIBITION EFFECTS OF KOH

Potassium containing salts such as K_2SO_4 and KNO_3 have been known to be capable of inhibiting flames (Refs. 2-12). Alkali metal salts have been added to propellants/gun powders in an effort to reduce or eliminate afterburning in the rocket exhaust or to reduce muzzle flash in gun firing. Tailoring of such propellants for specific plume and performance characteristics

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has been done largely by empirical variation of additives in extremely costly testing. This approach is critically limited by the lack of fundamental knowledge of the underlying chemical mechanisms controlling the suppression process. (This was highlighted at a workshop on suppression kinetics of rocket afterburning and gun muzzle flash held at the US Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD, June 10-12,1986). This section of the report reviews recent work in the chemical kinetics of afterburning and the influence of additives on the production of ions in such flame systems.

CHEMISTRY OF FLAME SUPPRESSION

The afterburning of the rocket exhaust products, principally H_2 and CO, is a major cause of high plume signature and other related problems. Secondary combustion (afterburning) takes place when the sequence of chain branching chemical reactions (Ref. 2)

$$H + O_2 = OH + O$$
$$O + H_2 = OH + H$$

and the chain propagating reaction

$$OH + H_2 = H_2O + H$$

produces active free radicals H, OH and O faster than these radicals can be removed by chain terminating recombination reactions such as

$$H + H + M = H_2 + M$$
$$OH + H + M = H_2O + M$$

The burning of carbon monoxide, which takes place concurrently with that of hydrogen, tends to propagate the combustion sequence. The principal reaction (Ref. 12) controlling the oxidation of CO

$$CO + OH = CO_2 + H$$

simply replaces one active radical by another radical.

Potassium compounds have been demonstrated to be effective suppressants of exhaust afterburning for double base propellants for a considerable range of thrust levels (200 N-12 kN) (Refs. 2-4). There is no agreement on the inhibition mechanisms of potassium salts (Refs. 5-9).

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Hynes, Steinberg and Schoefield (Ref. 5) measured OH and Na concentrations in 10 oxygen rich flames by saturated- and low powered- laser induced fluorescence techniques. The flames were seeded with NaCl solutions using an ultrasonic nebulizer. A reaction mechanism of 20 potential reactions of Na, NaO_2 and NaOH in $H_2/O_2/N_2$ flames has been postulated to explain the observed /calculated species profiles in the flame. The concentrations of major species H_2O, O_2 were assumed equal to the equilibrium values. The concentrations of H and O were calculated from the measured OH concentration and assuming balanced chemistry for

$$H + O_2 = OH + O$$

$$O + H_2 = OH + H$$

$$OH + H_2 = H_2O + H$$
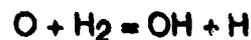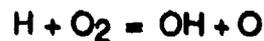
A simplified scheme made of four dominant reactions involving Na was able to predict the experimental data with sufficient accuracy:

$$Na + H_2O = NaOH + H$$

$$Na + O_2 + M = NaO_2 + M$$

$$NaO_2 + H = NaO + OH$$

$$NaOH + OH = NaO + H_2O$$
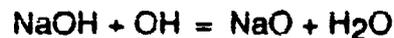
Heimerl (Refs. 6-9) has reported studies on the suppression of muzzle flash (similar to the afterburning phenomena in rocket exhausts) by the addition of potassium salts. Very little data concerning alkali salts suppressants at the elementary chemical level in actual gun systems are available. Results from several key laboratory experiments were reviewed for an alkali suppression mechanism and an elaborate mechanism (of up to 40 reactions) for suppression of $H_2/O_2/N_2$ flames seeded with K-salts was suggested. This mechanism has yet to be experimentally verified .

Friedman and Levy (Ref. 10) employed an opposed jet diffusion flame of CH_4 and O_2 in their experiment. They added atomic potassium to the fuel flow up to about 6% of the fuel and did not observe any quenching of the flame. They proposed that gaseous KOH is the species responsible for flame inhibition. It

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might act through reactions such as:

$$KOH + H = H_2O + K$$

$$KOH + OH = H_2O + KO$$

McHale (Ref. 11) studied afterburning suppression using solid rocket propellants formulated with known amounts of selected potassium salts. For K_2SO_4, $KHCO_3$ and $K_2C_2O_4$, he observed the intensity of 4.09 μ m CO_2 bands to decrease by a factor of 15 relative to the unsuppressed case. The addition of KBF_4 to the rocket propellant did not change the intensity of CO_2 bands. The computation of the equilibrium species distribution for effective suppressants species (K_2SO_4,$KHCO_3$,$K_2C_2O_4$) showed that either K or KOH, or both are important species containing potassium. The equilibrium distribution for KBF_4 (which is not an effective suppressant of the afterburning) showed that neither KOH nor K are important potassium containing species. Relying on the results of Friedman and Levy (Ref. 10), McHale concluded that KOH is the important suppressant species.

Cohen and Decker (Ref. 13) performed shock-tube experiments to determine the effect of KOH, K_2SO_4 and KNO_3 on the inhibition of H_2/O_2 explosions. Inhibition and suppression were observed in experiments involving KOH (presumed in the gas phase), but not involving K_2SO_4 or KNO_3 , both in the form of particulates. This work confirms McHales (11) inference about the importance of KOH and indicate that KNO_3 or K_2SO_4 routinely employed as flash suppressants must first be converted physically or chemically before being effective.

Jensen, Jones and Mace (Ref. 3) studied the flame inhibition by adding potassium in the form of potassium dipivaloylmethane, to a premixed $H_2/O_2/N_2$ flame. They monitored the temperature profile and hydrogen atom profile in the recombination region above the flame. They observed a decrease in hydrogen atom concentrations with increasing amount of suppressant. Jensen et. al. (Ref. 4) assumed a two step suppressant mechanism:

$$K + OH + M = KOH + M$$

$$KOH + H = H_2O + K$$
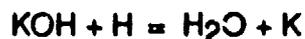
and by fitting the observations, they deduced an expression for these rate

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coefficients. The analysis of 10 fuel lean $H_2/O_2/N_2$ flames seeded with NaCl by Hynes et al. (Ref. 5) showed that the reaction $K + OH + M = KOH + M$ does not make significant contributions to the analogous reactions of Na salts. The value of the rate constant used for the backward reaction for this case used by Jensen et al. (Ref. 3) seems to be in error according to Hynes et al. (Ref. 5).

There appears to be a contradiction between the experimental results of Friedman and Levy (Ref. 10) and Jensen et al. (Ref. 14). The experiments may be sufficiently different and sufficiently complex that their results are correct in different operating ranges (Ref. 6). Recent work by Hynes, Steinberg and Schoefield (Ref. 5) shows that the reaction mechanism could be quite complex (20 potential reactions). Heimerl (Ref. 6) has suggested a mechanism consisting of 40 reactions for $H_2/O_2/N_2$ flames seeded with potassium salts. These studies do not take into account the ionization reactions which may be occurring simultaneously in $H_2/O_2/N_2$ flames seeded with K-salts. The feasibility of these mechanisms needs to be theoretically and experimentally investigated and will to be discussed in a later work.

STUDIES RELATED TO IONIZATION IN FLAMES

A number of studies have been reported on the rate of chemi-ionization in the laboratory flames. Most of these studies have been performed for hydrocarbon flames. Carabetta and Porter (Ref. 14) measured concentration of positive ions in $CO/O_2/N_2$ flames seeded with Na, K, Cs salts. Electrical probes were used for measuring positive ion concentrations. Peters and Van Tiggelen (Ref. 15) determined the overall rate of chemi-ionization in $CH_4/O_2/N_2$ flames. They also used electrical probes for monitoring the concentrations of positive ions. Traverse and Williams (Ref. 16) have discussed in detail the theory and use of electrical probes in flame plasmas. Maclatchy and Forsman (Ref. 17,18) have demonstrated the use of a double probe (one probe acts as a reference probe and the other acts as the test probe) for measuring ion density in propane air flames seeded with NaOH .

Cousins and Jensens (Ref. 19) have reported the computation of ionization levels in the rocket exhaust. The basic combustion mechanism for $H_2/CO/air$ flames was combined with the following reactions assumed to govern the production and removal of the charged species:

$$K^+ + e^- + M = K + M \tag{1}$$

$$K^+ + Cl^- = K + Cl \tag{2}$$

$$K^+ + Cl^- + M = KCl + M \tag{3}$$

$$K + H_2O = KOH + H \tag{4}$$

$$K + OH + M = KOH + M \tag{5}$$

The rate at which the reverse step proceeds for reaction 3 depends on the specific concentration of KCl and is linked to K concentration through the reaction :

$$K + HCl = KCl + H \tag{6}$$
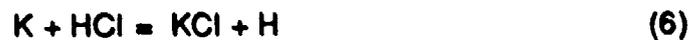
Reaction 6 was found to be close to equilibrium. Electron attachment and detachments are assumed to be affected through the following reactions (Ref.19):

$$HCl + e^- = Cl^- + H \tag{7}$$

$$Cl + e^- + M = Cl^- + M \tag{8}$$
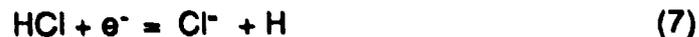
Reaction 7 was found to be the controlling reaction for the ratio $[Cl^-]/[e^-]$ and was close to the stoichiometric balance in a rocket exhaust. Cousins and Jensen's (Ref. 19) calculated values of e^- concentration were found to be dependant on hydrogen atom concentrations, which in turn were linked to the concentration of other radicals. The following bi-molecular reactions were found to be nearly balanced:

$$OH + H_2 = H_2O + H \tag{9}$$

$$O + H_2 = OH + H \tag{10}$$

$$OH + OH = H_2O + O \tag{11}$$

$$H_2O + Cl = HCl + OH \tag{12}$$
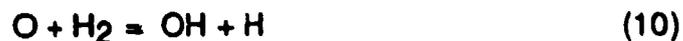
The computed concentration of hydrogen atoms was found to be above equilibrium by a factor of approximately 30 at the nozzle exit. In addition, this concentration was found to be above equilibrium by a factor of 3-4 in the hottest, near stoichiometric, region of the flame.

The calculations for the charged species were done for the exhausts of two rocket motors. The first motor contained K, Na and Cl salts as fuel impurity species, while the second motor had K, Na and Ca salts for the fuel impurities. The noise power, expressed in relative db per 1 Hz bandwidth, were computed for the motor exhaust under a set of specified conditions consistent with some known data firings. The computed results were found to agree within about ± 15 db with the experimental observations reported in an unpublished work (Ref. 19). The differences were attributed to uncertainties in the specific rate constants for radical recombination reactions and the ionization reactions.

It was further noted in these studies that high electron concentrations are achieved in the hottest part of the exhaust and that microwave radiation traversing these plume sections are heavily absorbed. Further, charged species concentrations including e^- concentrations in the outer parts of the exhaust are all well above the expected equilibrium levels. Finally, electron attachment reactions in the outer, oxygen rich regions dominate. This fact is true in particular for composite and double base propellants and should be taken into account. Some of the reactions detailing these conditions are presented below:

$$OH + e^- + M = OH^- + M \qquad (13)$$

$$H_2O + e^- = OH^- + H \qquad (14)$$

$$O_2 + e^- + M = O_2 + M^- \qquad (15)$$

$$O_2^- + OH = OH^- + O_2 \qquad (16)$$
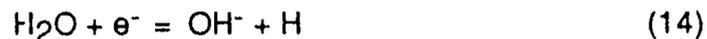
The rate coefficient for all of these reactions have substantial uncertainties.

COMPUTATIONAL MODEL

The experimental program needs to be supported by a computational model. A computer code for simulating the composition profile and temperature profile in one dimensional flat flame was obtained from the Sandia National Laboratory (Ref. 20). This program was developed by Kee, Grcar, Smooke and

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Miller of the Sandia National Laboratory. The program accounts for the finite rate chemical kinetics and molecular transport. Finite difference approximations are made to discretize the governing conservation equations on a non-uniform grid from the cold boundary to the hot boundary. The Newton method is used for solving the boundary value problem. Global convergence of this algorithm is aided by invoking the time integration procedures when the Newton method has convergence difficulties (Ref. 20).

CHEMICAL KINETIC MECHANISM

An eleven step reaction mechanism (Table 1) is used for simulating the base $H_2/O_2/N_2$ flames. This mechanism has been shown to give good agreement between the computed results and the corresponding experimental data (Refs. 21,22). This mechanism has been used by Zacharia and Smith (Ref. 23) to simulate sulfur chemistry in rich $H_2/O_2/SO_2$ flames, and by Coffee to simulate H_2/N_2O flames (Ref. 24). Added is a 15 step kinetic mechanism to describe the influence of potassium inhibition (equations 12-26).

TABLE 1

Reactions	Pre Exp A	Temp Exp b	Act Enrg* E
1. $H + O_2 = OH + O$	1.2E17	-0.91	16422.
2. $O + H_2 = OH + H$	1.5E07	2.00	7542.0
3. $OH + H_2 = H_2O + H$	1.0E08	1.60	3295.0
4. $2OH = O + H_2O$	1.5E09	1.14	0.0
5. $H + H + M = H_2 + M$	2.0E18	-1.00	0.0
6. $H + OH + M = H_2O + M$	2.2E21	-2.00	0.0
7. $H + O_2 + M = HO_2 + M$	2.0E18	-0.80	0.0
8. $H + HO_2 = 2OH$	1.5E14	0.00	1003.0
9. $H + HO_2 = H_2 + O_2$	2.5E13	0.00	692.0
10. $O + HO_2 = OH + O_2$	2.0E13	0.00	0.0
11. $OH + HO_2 = H_2O + O_2$	2.0E13	0.00	0.0
12. $H + KOH = K + H_2O$	1.0E13	0.00	1984.0
13. $K + OH + M = KOH + M$	0.54E21	-1.00	0.0
14. $K + O_2 + M = KO_2 + M$	0.50E18	-1.00	0.0
15. $H_2 + KO = H + KOH$	0.72E13	0.00	0.0
16. $H + KO_2 = OH + KOH$	1.0E13	0.00	0.0
17. $KO + H_2O = OH + KOH$	1.0E13	0.00	0.0
18. $H + KO_2 = KOH + O$	1.9E12	0.00	0.0
19. $H + KO_2 = K + HO_2$	1.9E12	0.00	0.0
20. $K + HO_2 = KO + OH$	1.9E12	0.00	0.0
21. $O + KO_2 = KO + O_2$	1.9E12	0.00	0.0
22. $KO + KO = K + KO_2$	1.0E13	0.00	0.0
23. $H + KH = K + H_2$	1.0E13	0.00	0.0
24. $KH + OH = K + H_2O$	1.0E13	0.00	0.0
25. $KH + O_2 = K + HO_2$	1.0E13	0.00	0.0
26. $H + KO_2 = KH + O_2$	1.0E13	0.00	0.0

*The rate coefficients are expressed as $k = AT^b \exp(-E/RT)$ in cm-mole-sec-calories units

The associated thermodynamic data and transport data for $H_2/O_2/N_2$ species have been compiled by Kee et al. (Ref. 25) and were used for these computations. The thermodynamic data and the transport data for K-species have been taken from the work of Heimerl (Ref. 7). For each species the

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molecular mass, the Lennard-Jones collisional diameter (in Angstroms), the Lennard-Jones potential well depth (in Kelvins), the dipole moment (in Debyes), the polarizability (in cubic Angstroms), and 14 thermodynamic parameters for use in the polynomial fits of Gordon and McBride (Ref. 26) have been compiled. The forward rate constants for $H_2/O_2/N_2$ reactions have been taken from Ref. 22. The rate data for K-reactions have been taken from Refs 6 and 7. The backward rate constants are calculated from the forward rate constants and the equilibrium constants (based on associated thermodynamic data). There is a large degree of uncertainty associated with the rate constants involving K-reactions.

The rate constant for the reaction $K + OH + M = KOH + M$ has been estimated to be $5.4E20\ T^{-1}$ $cm^6/mole^2/sec$ by Jensen, Jones and Mace (Ref. 3). This result was derived from their temperature and composition profile measurements in a $H_2/O_2/N_2$ flame seeded with K-salt and supported on a flat-flame burner. The recent measurements of Husain et al. (Ref. 27) show this value to be $4.7E21/T^{1.28}$ $cm^6/mole^2/sec$. We used a value of $5.4E20\ T^{-1}$ for the rate constant of this reaction for baseline calculations and varied it up to $5.4E21$ T^{-1} in our computations.

The rate data for the reaction $K + O_2 + M = KO_2 + M$ has been measured over the temperature range of 300-800 K. Silver et. al. (Ref. 28) recommend a value of $0.478E20\ T^{-0.6}$ while Husain et al. (Ref. 29) recommend a value of $0.5E18\ T^{-1}$ $cm^6/mole^2/sec$ for this reaction. Hynes et al. (Ref. 5) recommend a value of $.72E18\ T^{-1}$ for the corresponding analog reaction ($Na + O_2 + M = NaO_2 + M$) of Na system . A value of $0.5E18\ T^{-1}$ was used for the rate constant of this reaction for baseline computations and has been varied up to $0.5E21T^{-1}$.

The rate constant for $H + KOH = K + H_2O$ was estimated to be $1.0E13$ $exp^{(-1984/RT)}$ by Jensen and Jones (Ref. 3) and this value has been used in our computations. Very little data is available for the rest of the K-species reactions. Their rates have been estimated to vary from $1.0E11$ to $1.0E14$ $cm^3/mole/sec$ (Ref. 7).

IONIZATION EFFECTS

The addition of potassium salts to flames leads to a varying degrees of ionization depending on the temperature and concentration of K-salts present. A summary of the literature related to chemi-ionization in flames has been presented. For this work, the sensitivity of various ionization reactions has been

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studied by adding one reaction at a time to the 26 step reaction mechanism shown in Table 1. For potassium salts, the primary reactions governing the production and removal of charged species are presented below (Ref. 19) :

$$K^+ + e^- + M = K + M \tag{17}$$

$$K^+ + Cl^- = K + Cl \tag{18}$$

$$K^+ + Cl^- + M = KCl + M \tag{19}$$

For the addition of KOH, the reaction $K^+ + e^- + M = K + M$ would be most significant. In this reaction the rate constant is equal to 1.44E22 T^{-1} with an uncertainy factor of 30 (Ref. 19). The computed peak electron concentration mole fractions determined by the addition of Table 1 reaction 17 to the 26 step reaction mechanism are summarized in Table 2. These computations were performed for various equivalence ratios ranging from fuel-rich to fuel-lean conditions.

TABLE 2

H$_2$/O$_2$/N$_2$/KOH Ratio	Peak e⁻ Mole Frcn	Burn Vel cm/s
	Ø=2.38	
.50/.10/.39/.00001	1.189E-10	257.7
.49/.10/.39/.005	1.210E-07	236.9
.49/.10/.39/.010	2.400E-07	216.4
.49/.10/.39/.015	3.250E-07	196.4
.49/.10/.39/.020	3.790E-07	176.7
	Ø=0.79	
.25/.16/.59/.001	1.800E-08	167.5
.25/.16/.59/.005	1.610E-07	149.7
.25/.16/.59/.010	3.360E-07	128.1
	Ø=1.28	
.35/.14/.51/.00001	2.650E-09	262.4
.35/.14/.51/.0001	2.800E-08	261.6
.35/.14/.51/.001	4.890E-07	259.0
.35/.14/.51/.005	4.880E-06	244.9
.35/.14/.51/.01	8.800E-06	226.7
.34/.13/.50/.015	1.010E-05	205.3
.34/.13/.50/.020	1.020E-05	189.9

From Table 2 and Figs 1 - 3, it is seen that peak electron mole fraction increases as the mole fraction of KOH increases in the unburnt mixture for both fuel rich and fuel lean mixtures. This trend is opposite that exhibited by burning velocity, as shown in Figs 4 - 6, which is seen to decrease as the KOH mole fraction increases in the unburnt mixture. Thus, it is seen that as the inhibition effect of K-salt (seen as a decrease in burning velocity and peak OH mole fraction) increases, the peak mole fraction of electron concentration increases.

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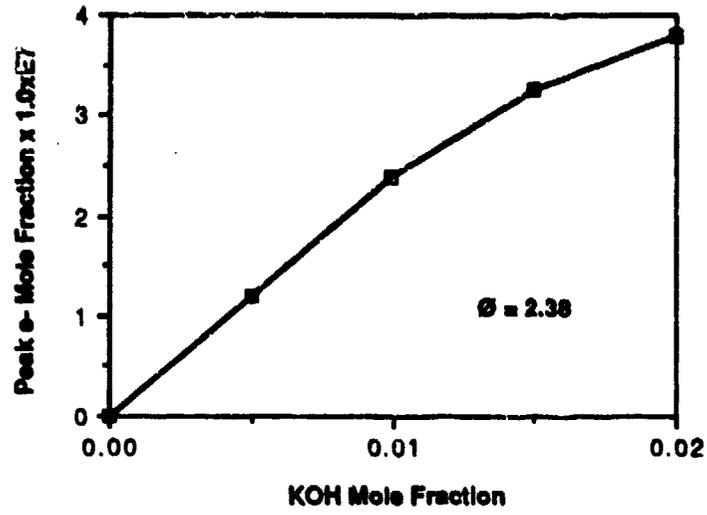
Figure 1. Peak [e-] vs KOH Mole Fraction
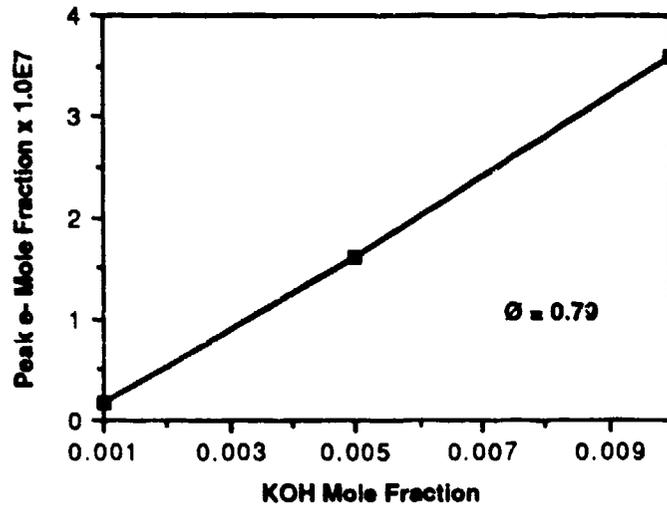

Figure 2. Peak [e-] vs KOH Mole Fraction

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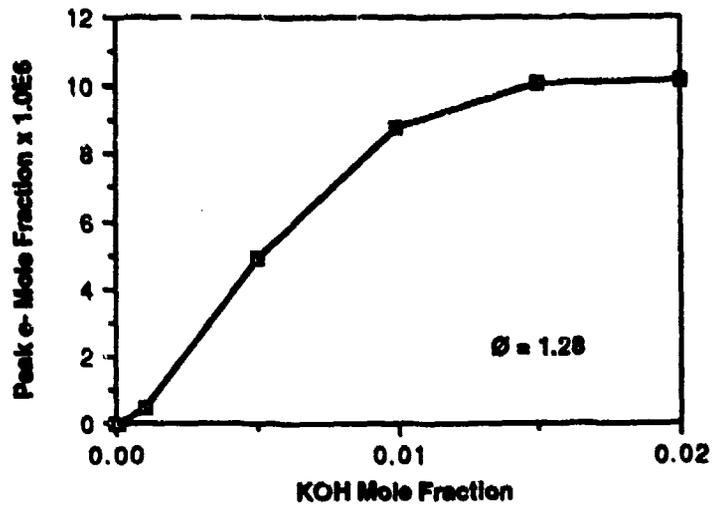
Figure 3. Peak [e-] vs KOH Mole Fraction
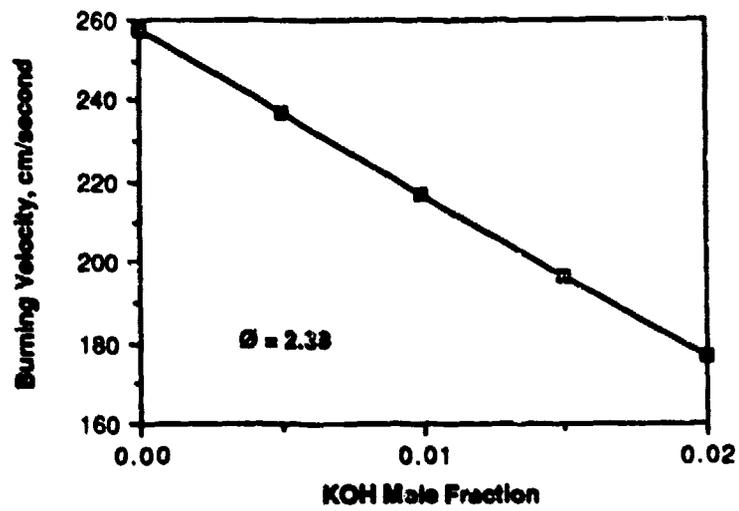

**Figure 4. Burning Velocity vs [KOH]**

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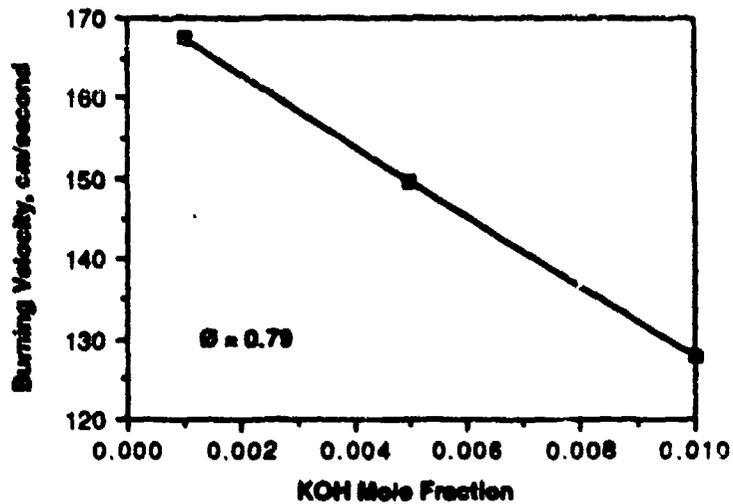
Figure 5. Burning Velocity vs [KOH]
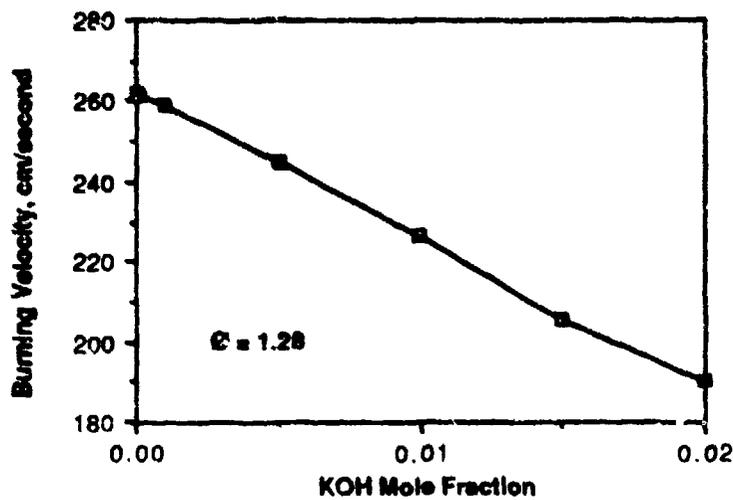
Figure 6. Burning Velocity vs [KOH]

As was discussed earlier, the rate constants for the K-reactions have a high level of uncertainty. The sensitivity of various key reactions and their influence on the peak electron mole fraction was examined by changing the pre-exponential factor of the individual rate constants one at a time. The results for these reactions are given below:

REACTION - $K^+ + e^- + M = K + M$

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Fig. 7 shows the sensitivity with respect to rate constant for the reaction $K^+ + + e^- + M = K + M$. As the pre-exponential factor for this reaction is increased by three orders of magnitude, the peak electron mole fraction increases by a factor of about 8.5. The rate of change for peak electron mole fraction is smaller as the rate constant pre-exponential factor is increased from 1.0E23 to 1.0E24, as compared to the increase from 1.0E22 to 1.0E23.
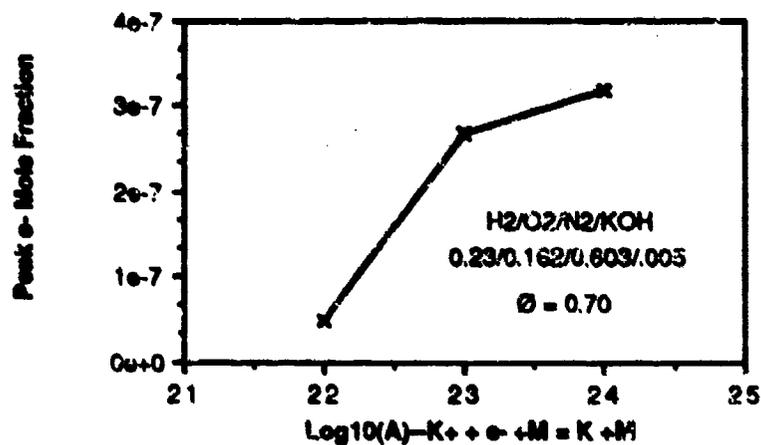
**Figure 7. Peak e- Concentration vs Rate Constant**

REACTION $H + KOH = K + H_2O$

From Fig. 8 it is seen that the computed peak electron mole fraction increases as the pre-exponential factor for this rate constant is increased by two orders of magnitude for various concentration levels of KOH at $\emptyset = 2.38$. The increase in the rate constant for the reaction $H + KOH = K + H_2O$ also results in a decrease in the burning velocity. This means an increase in the inhibition effect.
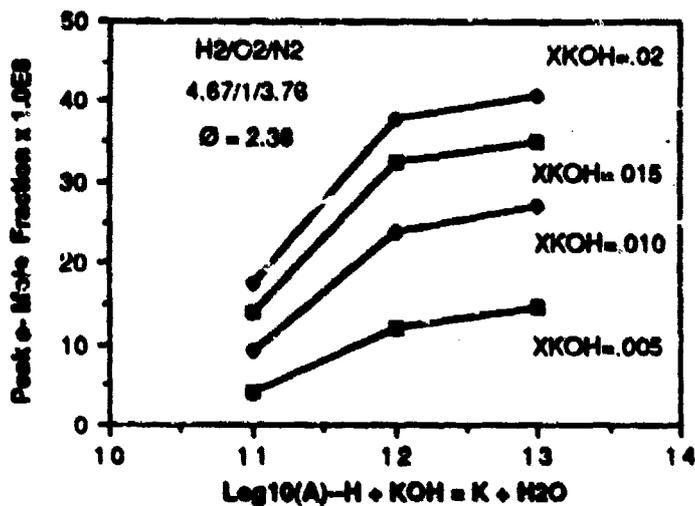
Figure 8. Peak [e-] vs Reaction Rate

REACTION K + OH + M = KOH + M

Fig. 9 shows that the computed peak electron mole fraction again increases with the rate constant increase for the reaction K + OH + M = KOH + M. These results are shown for various concentrations of added KOH. The burning velocity decreases (the inhibition effect increases) as the rate constant for this reaction increases.
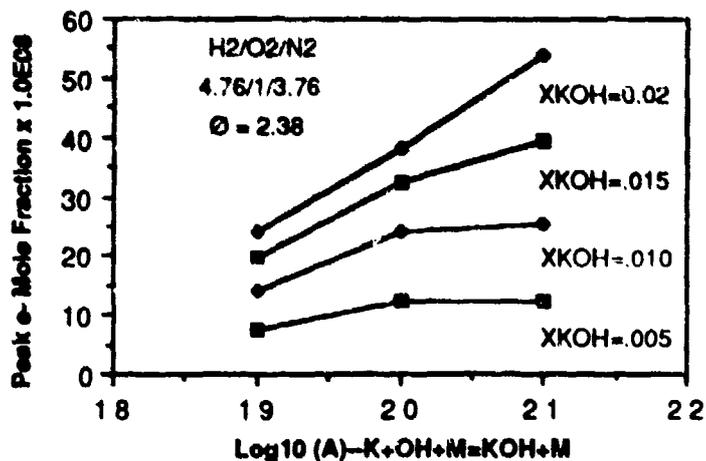

Figure 9. Peak e- Concentration vs Rate Constant

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REACTION K + O₂ + M = KO₂ + M

Fig. 10 shows that the computed peak electron mole fraction decreases slightly as the rate constant for this reaction is increased. The burning velocity increases as the rate constant increases. This is equivalent to a decrease in the effect of inhibition as the rate constant ncreases.
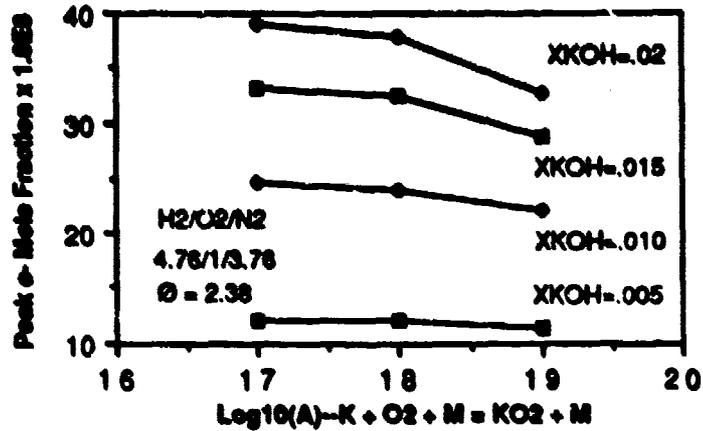

Figure 10. Peak [e-] vs Reaction Constant

From the above analysis it can be seen that the peak electron concentration is proportional to the inhibition effect. The inhibition effect is identified by a decrease in burning velocity with an accompanying decrease in the peak OH mole fraction of flames to which potassium containing salts have been added.

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In the above analysis it can be seen that the chemical kinetic mechanisms controlling flame inhibition can be modelled and connected to those responsible for ion production in a flame seeded with potassium salts in low concentrations. As can be seen, the desired chemical kinetic influence in the flames of interest can be obtained by selectively manipulating the available radical pool to control and distribute the released heat and to simultaneously minimize the production of ions. In order to illustrate this point graphically, a series of computations were performed using the 26 step reaction mechanism shown in Table 1. To this mechanism was added the reaction $K^+ + e^- + M = K + M$. This reaction is most significant in its influence in the reaction scheme when KOH is added to the flame. Table 3 presents results for equilibrium mole fraction of e^-, flame speed, and flame temperature for the cases where potassium is added as 1) atomic potassium or 2) KOH. These results are shown graphically in Figs. 11 - 13.

TABLE 3

K	Temperature, K (Initial K as)		e- Equilibrium Mole Fraction*		Flame Speed, cm/sec (Initial K as)	
Percent	K	KOH	K	KOH	K	KOH
0.0	2017	2017	0.0	0.0	236.7	236.7
1.0	2024	1990	3.429	3.857		175.0
2.0	2032	1963	6.571	2.857	163.3	125.0
3.0						83.3
4.0					106.7	30.0
5.0	2050	1934	7.190	1.286	88.3	30.0
7.0			9.095	1.238		

* Mole Fraction Approximately E^{-10}.

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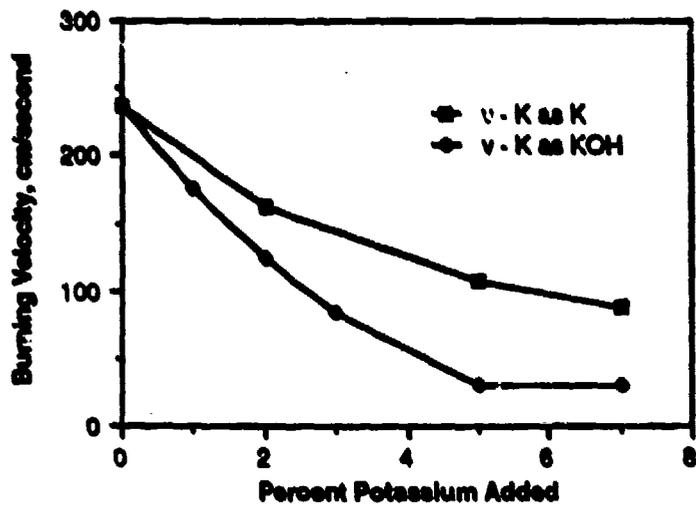
**Figure 11. Burning Velocity vs Potassium Added**
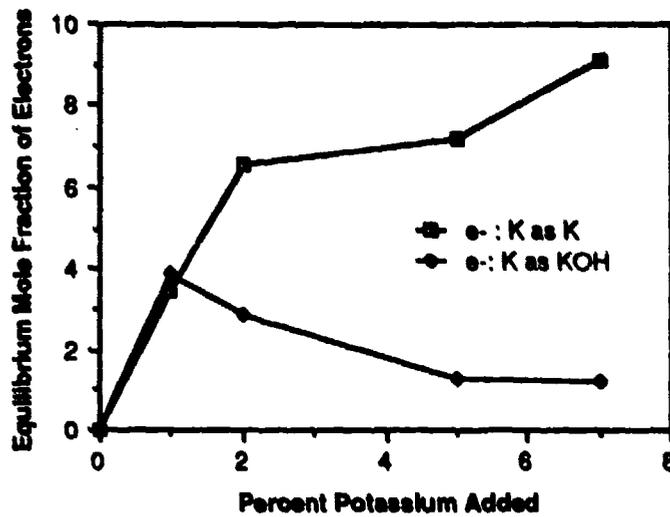
**Figure 12. Mole Fraction e- vs Potassium Added**

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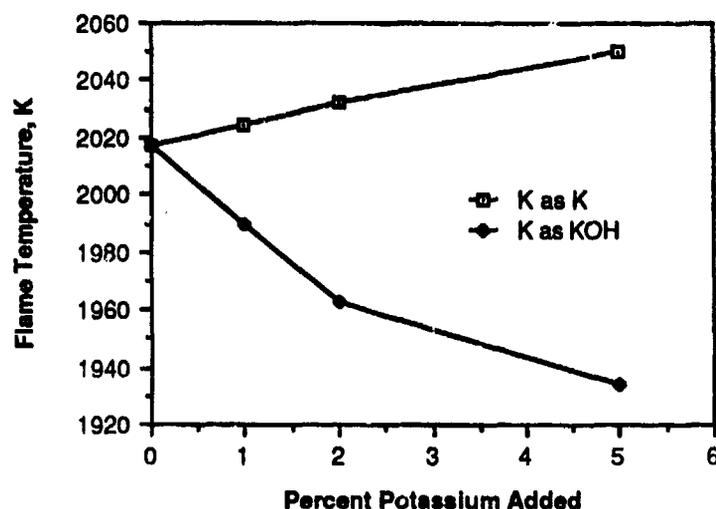
Figure 13. Flame Temperature vs Potassium Added

As the concentration of potassium is increased from 0 to 5% in the unburnt fuel mixture, the equilibrium adiabatic flame temperature increases from 2017 K to 2050 K. The corresponding equilibrium mole fraction of free electrons (e^-) changes from approximately E^{-10} to $9.095E^{-7}$. If the potassium is present bound as KOH, then the equilibrium adiabatic flame temperature decreases from 1990 K to 1934 K as the percentage of KOH in the unburnt fuel mixture increases from 1 to 5. The corresponding equilibrium mole fraction of free electrons peaks at $3.857 E^{-7}$ for the addition of 1% KOH and then decreases. Hence the ability to control collectively the inhibition effect and th $\cdot$ e^- concentration.

SUMMARY AND CONCLUSIONS

•The chemical kinetic mechanisms controlling flame inhibition and the production of ions in a hydrogen-oxygen flame seeded with potassium has been modelled. An 11 step kinetic reaction model was used for computing the structure of the base hydrogen-oxygen flame. Fifteen additional reactions for the addition of KOH were used to simulate the inhibition effects. Additional individual reactions were added to this mechanism one at a time to evaluate the degree of ionization induced by the introduction of potassium salts to the unburned fuel mixture.

•The laminar burning velocity and peak mole fraction of H and OH decrease as the mole fraction of potassium seed increases in the unburnt

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mixture. This observed trend was similar for both fuel-lean and fuel-rich flames.

•The peak electron concentration was found to be proportional to the potassium salt inhibition effect.

•Selective manipulation of the available radical pool can be used to distribute the released heat within the flame for the purpose of inhibition while at the same time minimizing the production of ions (in this case free electrons).

•The particular mechanism used in the process of flame inhibition can be the key in limiting ion production. The use of KOH as an inhibitor can provide successful inhibition at 3% suppressant addition, while simultaneously controlling electron production when compared to the use of K as the inhibitor.

•The suggested mechanism can be used to evaluate the specific increase in electron concentration with suppressant addition. Evaluation of the optimum degree of suppression and specific level of electron production can be performed.

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